Volumetric Ion Interaction Parameters for Single-Solute Aqueous Electrolyte Solutions at Various Temperatures

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The ion interaction approach developed by Pitzer allows the prediction of thermodynamic characteristics of mixed electrolyte solutions at various temperatures, if the respective parameters for each type of single electrolyte solution are known. Among such thermodynamic characteristics are the volumetric ones (density and apparent molal volumes). A database for the densities and the apparent molal volumes versus concentrations was developed at a temperature interval of 288.15–368.15 K using all available literature sources for each single electrolyte solution formed by various electrically neutral combinations of the following ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-}). These are the most important ions for industrial solutions as well as for natural waters. Statistical treatment was applied to this database in order to discard poor data. The proper treatment of all sound quality apparent molal volumes, in a wide range of concentrations from infinite dilution through saturation, allowed us to compute sets of volumetric ion interaction parameters ($\bar{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX}) at various temperatures in a 288.15–368.15 K temperature interval. The validity of the selected sets at various temperatures was demonstrated by a comparison of the experimental and calculated densities for multiple-solute electrolyte solutions containing NaCl, KCl, $MgCl_2$, and $CaCl_2$ with an ionic strength reaching 9.23 that resembled Dead Sea water. © *2001 American Institute of Physics.* [S0047-2689(00)00105-7]

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[c)]This work is dedicated to the memory of the late Professor Kenneth Pitzer who passed away on December 26, 1997.

1. Introduction

Pitzer and his scientific school [(1973), (1979), (1991), and references therein] suggested a semiempirical model allowing the prediction of various thermodynamic properties of multiple-solute electrolyte solutions by using so-called ion interaction parameters which can be calculated from appropriate experimental data for single-solute and ternary electrolyte solutions at various temperatures. Among such properties are volumetric ones (solution density and apparent molal volumes of solutes) whose most important application is calculating the pressure effects on ionic activity coefficients, on the osmotic coefficients, on mineral solubility, etc. The required volumetric characteristics for these types of calculations can be obtained by measuring part of these characteristics experimentally (such as densities), or by computing them (apparent and partial molal volumes, etc.) on the basis of experimentally verified models. Most papers published in the last decade which dealt with the application of the Pitzer approach for calculations of volumetric characteristics of electrolyte solutions were related to a fixed temperature of 298.15 K and were reviewed by us earlier [Krumgalz *et al.* (1996)]. If one needs to calculate the density of an aqueous multiple-solute electrolyte solution or hypersaline natural waters, or the apparent molal volume of a solute in these types of systems at temperatures other than 298.15 K, it is often impossible to find an entire complete satisfactory set of volumetric ion interaction parameters from the limited amount of available parameters published.

The values of the Pitzer volumetric ion interaction parameters ($\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V) for single-solute electrolyte solutions at temperatures other than 298.15 K have been reported in several publications during the last decade [Rogers and Pitzer (1982); Kumar and Atkinson (1983); Atkinson *et al.* (1986); Connaughton *et al.* (1986), (1989); Grzybkowski and Atkinson (1986); Kumar (1986a), (1986b), (1986c); Connaughton and Millero (1987); Kumar (1987a), (1987b); Monnin (1987), (1990); Pabalan and Pitzer (1987); Dedick *et al.* (1990)]. Although these papers were excellent for their purpose at that time, there are significant differences among the volumetric ion interaction parameters reported for particular electrolytes. Also, in a few cases [Kumar *et al.* (1982); Atkinson *et al.* (1986); Grzybkowski and Atkinson (1986); Kumar (1986b)] some of equations that

were used differed from the commonly accepted equation developed by Rogers and Pitzer (1982). Thus, it is worth while making new calculations using the correct equation and all reliable experimental density data for these particular solutes.

Krumgalz *et al.* (1995) recently developed the first approximation of the Pitzer approach allowing the prediction of volumetric properties of mixed electrolyte solutions 298.15 K by using volumetric ion interaction parameters calculated from appropriate experimental data for single and ternary electrolyte solutions. The approach discussed proved very effective at 298.15 K for volumetric calculations related to natural hypersaline brines and very complex industrial electrolyte solutions. In this paper, we will develop a similar approach at a wider temperature interval of 288.15–368.15 K. This paper will deal only with mixed electrolyte solutions formed by electrically neutral combinations of ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, Br^-, HCO_3^-, CO_3^{2-} and SO_4^{2-}). Our choice of these ions was based on the fact that they are most important for complex industrial solutions as well as those having particularly important interest for describing the geochemical evolution of natural waters.

The current paper has several objectives:

(1) to develop a database of density and apparent molal volumes at a 288.15 and 368.15 K temperature interval for single electrolyte solutions available in literature;
(2) to conduct rigid statistical analysis of the developed database;
(3) to compute anew the values of the Pitzer volumetric ion interaction parameters ($\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V) as functions of temperature at intervals of 288.15–368.15 K by using the most reliable density and apparent molal volume data from the developed database; and
(4) to verify the obtained Pitzer volumetric ion interaction parameters ($\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V) at various temperatures on existing density data for mixed solutions.

2. Ion Interaction Model for the Volumetric Properties of Single-Solute Electrolyte Solutions

When developing the first approximation of the Pitzer ion interaction model, only the pairwise interactions of unlike charged ions are taken into consideration. The model allows calculating the basic volumetric parameters for electrolyte solutions, such as solution densities "ρ" and apparent molal volume values of a solute "$V_{\phi,MX}$," which are defined as

$$V_{\phi,MX} = \frac{V - n_1 \cdot V_1^0}{n_2} = \frac{1000 \cdot (\rho_0 - \rho)}{m \cdot \rho \cdot \rho_0} + \frac{M}{\rho},$$

$$\rho = \frac{1000 + m \cdot M}{(1000/\rho_0) + m \cdot V_{\phi,\mathrm{MX}}}, \qquad (2)$$

where ρ_0 is the mass density of a pure solvent; m is the molal concentration of a solution; n_1 and n_2 are the numbers of moles of a solvent and of a solute in the solution, respectively; V and V_1^0 are the molal volumes of a solution and a solvent, respectively, both at the same absolute temperature (T) and pressure (P); M is the molecular mass of the solute MX. The molal volume of a solution is given by the first pressure derivative of the total Gibbs energy of the solution [Pitzer (1991)]:

$$V = (\partial G/\partial P)_T$$

$$= \{\partial[n_1 \cdot G_1^0 + n_2 \cdot \bar{G}_2^0 + G^{\mathrm{ex}}$$

$$+ n_2 \cdot \nu \cdot R \cdot T \cdot (\ln m - 1)]/\partial P\}_{T, n_1, n_2}, \qquad (3)$$

where G_1^0 and $\bar{G}_2^0 \equiv \bar{G}_{\mathrm{MX}}^0$ are the molal Gibbs free energy of a pure solvent and the partial molal Gibbs free energy of a solute at infinite dilution, respectively; G^{ex} is the excess Gibbs molal free energy of a solution; ν is the number of ions forming a solute molecule, and R is the gas constant. Henceforth, it is understood that all partial differentials are carried out with n_1 and n_2 kept constant. Differentiating Eq. (3) yields

$$V = n_1 \cdot \left(\frac{\partial G_1^0}{\partial P}\right)_T + n_2 \cdot \left(\frac{\partial \bar{G}_2^0}{\partial P}\right)_T + \left(\frac{\partial G^{\mathrm{ex}}}{\partial P}\right)_T$$

$$= n_1 \cdot V_1^0 + n_2 \cdot \bar{V}_2^0 + \left(\frac{\partial G^{\mathrm{ex}}}{\partial P}\right)_T$$

$$= n_1 \cdot V_1^0 + n_2 \cdot \left(\bar{V}_2^0 + \frac{\Delta V^{\mathrm{ex}}}{n_2}\right), \qquad (4)$$

where $\bar{V}_2^0 \equiv \bar{V}_{\mathrm{MX}}^0$ is the partial molal volume of a solute at infinite dilution and ΔV^{ex} is the excess volume. Substituting Eq. (4) into Eq. (1) gives

$$V_{\phi,\mathrm{MX}} = \bar{V}_{\mathrm{MX}}^0 + \frac{\Delta V^{\mathrm{ex}}}{n_2} = \bar{V}_{\mathrm{MX}}^0 + \frac{1}{n_2} \cdot \left(\frac{\partial G^{\mathrm{ex}}}{\partial P}\right)_T. \qquad (5)$$

Substituting the equation for the first pressure derivative of the excess Gibbs free energy into the above equation yields the parametric form of the equation for the apparent molal volume of a solute. The excess Gibbs free energy of a system is the difference between the Gibbs free energy of the real system and that of an ideal system under the same conditions. The parametric equation suggested by Pitzer (1991) for the excess Gibbs free energy of a single-solute electrolyte solution containing 1 kg of solvent is defined as

$$G^{\mathrm{ex}} = R \cdot T \cdot \left[-A_\phi \cdot \left(\frac{4 \cdot I}{b}\right) \cdot \ln(1 + b \cdot I^{1/2}) + 2 \cdot m^2 \cdot \nu_M \cdot \nu_X \right.$$

$$\left. \cdot (B_{\mathrm{MX}} + \dot{m} \cdot \nu_M \cdot z_M \cdot C_{\mathrm{MX}}) \right], \qquad (6)$$

where ν_M and ν_X are the number of cations and anions in a solute molecule, respectively; I is the ionic strength of a solution and A_ϕ is the Debye–Hückel coefficient for the osmotic function [Pitzer (1991)]. The general form of the equations for the B_{MX} and C_{MX} terms can be presented as

$$B_{\mathrm{MX}} = \beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(I)} \cdot g(\alpha_1 \cdot I^{1/2}) + \beta_{\mathrm{MX}}^{(2)} \cdot g(\alpha_2 \cdot I^{1/2}), \qquad (7)$$

$$C_{\mathrm{MX}} = C_{\mathrm{MX}}^\phi / (2 \cdot |z_M \cdot z_X|^{1/2}), \qquad (8)$$

where b, α_1, α_2, $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$, $\beta_{\mathrm{MX}}^{(2)}$, and C_{MX} are the Pitzer ion interaction parameters; z_M and z_X are the charges of cations and of anions in a solute molecule, respectively; and a parameter $g(\alpha_i \cdot I^{1/2})$ is expressed as

$$g(\alpha_i \cdot I^{1/2}) = \frac{2}{\alpha_i^2 \cdot I} \cdot [1 - (1 + \alpha_i \cdot I^{1/2}) \cdot \exp(-\alpha_i \cdot I^{1/2})] \qquad (9)$$

The following numeric values of the coefficients in the above mentioned equations have been used: $b = 1.2 \, \mathrm{kg}^{1/2} \, \mathrm{mol}^{-1/2}$ for all charge type electrolytes; $\alpha_1 = 2.0 \, \mathrm{kg}^{1/2} \, \mathrm{mol}^{-1/2}$ for 1:1, 1:2, and 2:1 electrolytes; and $\alpha_1 = 1.4 \, \mathrm{kg}^{1/2} \, \mathrm{mol}^{-1/2}$ and $\alpha_2 = 12 \, \mathrm{kg}^{1/2} \, \mathrm{mol}^{-1/2}$ for 2:2 electrolytes; the coefficient $\beta_{\mathrm{MX}}^{(2)}$ was assumed to be equal to 0 for all charge type electrolytes except 2:2 electrolytes [Pitzer (1979)]. The coefficients α_1, α_2, and b were accepted to be temperature independent.

Substituting Eq. (6) into Eq. (5) and expressing n_2 in terms of m yields

$$V_{\phi,\mathrm{MX}} = \bar{V}_{\mathrm{MX}}^0 + \nu \cdot |z_M \cdot z_X| \cdot \left(\frac{A_V}{2 \cdot b}\right) \cdot \ln(1 + b \cdot I^{1/2})$$

$$+ 2 \cdot R \cdot T \cdot \nu_M \cdot \nu_X \cdot m \cdot [B_{\mathrm{MX}}^V + m \cdot \nu_M \cdot z_M \cdot C_{\mathrm{MX}}^V], \qquad (10)$$

where the coefficients A_V, B_{MX}^V, and C_{MX}^V are defined by

$$A_V = -4 \cdot R \cdot T \cdot \left(\frac{\partial A_\phi}{\partial P}\right)_T, \qquad (11)$$

$$B_{\mathrm{MX}}^V = \left(\frac{\partial B_{\mathrm{MX}}}{\partial P}\right)_T$$

$$= \beta_{\mathrm{MX}}^{(0)V} + \beta_{\mathrm{MX}}^{(1)V} \cdot \left(\frac{2}{\alpha_1^2 \cdot I}\right) \cdot [1 - (1 + \alpha_1 \cdot I^{1/2})$$

$$\cdot \exp(-\alpha_1 \cdot I^{1/2})] + \beta_{\mathrm{MX}}^{(2)V} \cdot \left(\frac{2}{\alpha_2^2 \cdot I}\right)$$

$$\cdot [1 - (1 + \alpha_2 \cdot I^{1/2}) \cdot \exp(-\alpha_2 \cdot I^{1/2})], \qquad (12)$$

where

$$\beta_{\mathrm{MX}}^{(i)V} = \left(\frac{\partial \beta_{\mathrm{MX}}^{(i)}}{\partial P}\right)_T, \qquad (13)$$

where $i = 0, 1, 2$, and $\beta_{\mathrm{MX}}^{(i)}$ are Pitzer ion interaction parameters for osmotic function.

$$C_{\mathrm{MX}}^V = \left(\frac{\partial C_{\mathrm{MX}}}{\partial P}\right)_T = \frac{(\partial C^\phi/\partial P)_T}{2 \cdot |z_M \cdot z_X|^{1/2}}, \qquad (14)$$

where $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^{V} are the Pitzer volumetric ion interaction parameters.

Temperature dependence of volumetric properties determined by the Pitzer model could be analyzed using Eqs. (1), (2), and (10). The following items in these equations are temperature dependent: $V_{\phi,MX}$, V_1^0, ρ_0, ρ, A_V, $\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^{V}.

The temperature dependence of pure water density in $g \cdot cm^{-3}$ at 1 atm pressure is determined by the equation developed by Kell (1975)

$$\rho_0 = (0.999\,839\,52 + 16.945\,176 \cdot 10^{-3} \cdot (T - 273.15)$$

$$- 7.987\,040 \cdot 10^{-6} \cdot (T - 273.15)^2$$

$$- 46.170\,461 \cdot 10^{-9} \cdot (T - 273.15)^3$$

$$+ 105.563\,02 \cdot 10^{-12} \cdot (T - 273.15)^4$$

$$- 280.542\,53 \cdot 10^{-15} \cdot (T - 273.15)^5) /$$

$$(1 + 16.879\,850 \cdot 10^{-3} \cdot (T - 273.15)). \tag{15}$$

One of the referees disagrees with our use of the 1975 water densities from Kell (1975) as obsolete ones. One of our reasons to use Kell's values in our calculations was the fact that in most works dealing with the density measurements of electrolyte solutions the values of pure water density used were either values from Kell (1975) or those close to them. We conducted some calculations by replacing Kell's equation (1975) for water density with the Haar *et al.* (1984) equation. The differences obtained were negligible compared with the precision of the apparent molal volume calculations.

The numerical values of the A_V (Debye–Hückel slope) for each 10 K in 298.15–648.15 K temperature interval were computed by Rogers and Pitzer (1982). For the convenience of using A_V values at any temperature in the temperature interval under study, we presented the calculated temperature dependence of A_V at a 273.15–393.15 K interval in the polynomial form of a temperature as a variable

$$A_V = 1.504\,15 + 1.3421 \cdot 10^{-2} \cdot (T - 273.15)$$

$$+ 3.0591.10^{-5} \cdot (T - 273.15)^2$$

$$+ 1.155\,88 \cdot 10^{-6} \cdot (T - 273.15)^3$$

$$- 5.2393 \cdot 10^{-9} \cdot (T - 273.15)^4$$

$$+ 2.6561 \cdot 10^{-11} \cdot (T - 273.15)^5. \tag{16}$$

Pitzer (1991) analyzed in detail the effect of the use of various values of water dielectric constant and the Debye–Hückel slopes on the precision of ion interaction parameter calculations. He concluded that for most purposes, any correction would not be significant and is not required. One of the referees cited the dielectric constant (ε) and Debye–Hückel volume slope (A_V) from Fernandez *et al.* (1997). The difference between A_V values from Rogers and Pitzer (1982) and from Fernandez *et al.* (1997) is relatively small and the error introduced by this difference in an apparent molal volume calculation is negligible. To collaborate this statement, we calculated the difference between the $V_{\phi,MX}$

values by using the Debye–Hückel volume slope $A = 1.875$ from Rogers and Pitzer (1982) and $A_V = 1.89$ from Fernandez *et al.* (1997) at 25 °C. This difference given as

$$\Delta V_{\phi,MX} = \nu \cdot |z_M \cdot z_X| \cdot \left(\frac{\Delta A_V}{2 \cdot b} \right) \cdot \ln(1 + b \cdot I^{1/2}). \tag{1}$$

Then for NaCl, for instance, $\Delta V_{\phi,MX} = 0.01_5 \, cm^3 \cdot mol^-$. Thus, the difference is significantly less than the errors $V_{\phi,MX}$ calculations by the Pitzer approach [Krumgalz *et c* (1996)].

The volumetric Pitzer ion interaction parameters $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V at various temperatures will be furth calculated in this paper from experimental apparent mol volumes of proper single-solute aqueous electrolyte sol tions.

3. Pitzer's Volumetric Ion Interaction Parameters at Various Temperatures

Pitzer's ion interaction approach in its first approximati(allows the prediction of various volumetric characteristics multiple-solute electrolyte solutions, if volumetric ion inte action parameters $\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V f each type of single-solute electrolyte solution are known. is understood that any attempt to describe thermodynam properties of multiple-solute electrolyte solutions (in partic lar, those of natural brines and mixed solutions in vario chemical industry branches) in terms of the Pitzer ion inte action parameters of certain relevant single-solute electroly solutions, can be justified only if all of the parameters ha been obtained by using the same methods. Therefore, sets volumetric ion interaction parameters that were comput(under either dissimilar definitions or by using dissimilar e perimental data processing methods are conceptually incc rect. Hence, none of these could be recommended as a ba: for further computations of either apparent molal volumes solution densities in multiple-solute electrolyte solutions, general and in natural brines, in particular. Thus, in order make the computation reliable, all volumetric ion interactii parameters should be determined by the same method.

In light of the above, the following three interrelated pro lems had to be solved in the current article:

(1) to create and statistically analyze a database of densiti and apparent molal volumes available in the literatu for single-solute electrolyte solutions at temperatui other than 298.15 K;

(2) to compute the volumetric ion interaction paramete ($\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V) at temperatui other than 298.15 K by using the most reliable densi and apparent molal volume data for single-solute ele trolyte solutions from the created database; and

(3) to make a comparative survey of all calculated values volumetric ion interaction parameters at temperatui other than 298.15 K by exposing them to a certain si tistical criterion of reliability. The best (most reliab values obtained in this manner will then be recoi

mended for further usage in the density and apparent molal volume calculations at temperatures other than 298.15 K.

3.1. Database of the Densities and Apparent Molal Volumes at Various Temperatures

Using essentially all published relevant data, a complete database for the densities and apparent molal volumes at temperatures between 288.15 and 368.15 K as a function of solute concentrations was created for each single-solute electrolyte solution under study. Table 1 lists the literature sources from which the densities and apparent molal volumes at various temperatures and only at a pressure of 1 atm have been taken for the creation of our databases. An attempt was made to cover all available information in the literature up to the end of 1996. However, in very rare cases, we expect that some papers could have been inadvertently over-

looked or were unavailable to the authors. We would appreciate any comments on missing papers. The density and apparent molal volume values as a function of the electrolyte concentration taken from the literature have been approximated by the least mean squares polynomial of the orders from 2 to 4 of the variable $m^{1/2}$ at each temperature. Higher statistical weight was attributed in all cases to the experimental data obtained by using new types of precise densimeters developed by Franks and Smith (1967), Millero (1967) and Picker *et al.* (1974), with a precision of density measurements reaching $2 \cdot 10^{-6}$ g·cm^{-3}. Values of the densities and apparent molal volumes deviated from the best-fit curve by two or more standard deviations were discarded from the databases. The reason for such deviations could be experimental errors in measuring both the solution concentrations and densities. Only the remaining data, whose values were consistent with one another, were included in our database for further consideration.

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for calculations of volumetric ion interaction parameters at various temperatures

| Solute | Temperature (K) | Concentration | | Literature source | Year |
		from	to		
NaCl	278.15–308.15	0.01	1.50	Chen *et al.*	1980
	278.15–368.15	2.87	3.43	Connaughton & Millero	1987
	288.15–308.15	0.001	0.51	Kaminsky	1957
	288.15–308.15	0.40	6.20	Kumar & Atkinson	1983
	288.15–318.15	0.003	0.93	Dunn	1968
	288.15–318.15	0.01	0.97	Millero	1970
	288.15–318.15	0.03	3.01	Perron *et al.*	1975
	288.15–318.15	0.06	5.92	Dessauges *et al.*	1980
	288.15–318.15	0.37	6.00	Lo Surdo *et al.*	1982
	288.15–328.15	0.05	5.00	Isono	1980
	288.15–328.15	0.10	1.20	Out & Los	1980
	293.15–313.15	0.10	5.80	Lengyel *et al.*	1964
	293.15–313.15	0.01	5.41	Millero & Drost-Hansen	1968
	298.15	0.35	5.70	Gibson	1934
	298.15	0.55	2.22	Lanman & Mair	1934
	298.15	0.02	0.69	Kruis	1936
	298.15	0.002	2.10	Jones & Christian	1937
	298.15	0.04	6.14	Wirth	1940
	298.15	0.50	4.51	Stakhanova & Vasilev	1963
	298.15	0.02	3.66	Vaslow	1966
	298.15	0.02	0.31	Millero	1967
	298.15	0.01	3.02	Fortier *et al.*	1974
	298.15	0.20	1.98	Picker *et al.*	1974
	298.15	0.01	5.83	Goncalves & Kestin	1977
	298.15	0.01	1.00	Millero *et al.*	1977
	298.15	0.06	2.81	Olofsson	1979
	298.15	0.99	5.95	Perron *et al.*	1981
	298.15	0.01	5.33	Simard & Fortier	1981
	298.15	0.30	5.00	Kumar *et al.*	1982
	298.15	0.06	5.00	Gates & Wood	1985
	298.15	1.00	4.00	Kumar	1985
	298.15	1.00	3.00	Millero *et al.*	1985
	298.15	0.30	1.00	Kawaizumi *et al.*	1988
	298.15	0.50	4.50	Kumar	1988b
	298.15	0.50	4.00	Kumar	1988a
	298.15	1.95	1.95	Dedick *et al.*	1990
	298.15–308.15	0.50	6.04	Oakes *et al.*	1990
	298.15–313.15	0.05	2.90	Allred & Woolley	1981
	298.15–318.15	1.00	6.10	Romankiw & Chou	1983

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for calculations of volumetric ion interaction parameters at vario temperatures—Continued

| Solute | Temperature (K) | Concentration | | Literature source | Year |
		from	to		
	298.15–323.15	0.26	6.04	Geffcken	1931
	298.15–323.15	0.13	2.01	Chen et al.	1977
	298.15–348.15	0.10	2.50	Fabuss et al.	1966
	298.15–348.15	0.10	3.54	Korosi & Fabuss	1968
	308.15	0.50	5.65	Scott et al.	1934
	308.15	0.11	1.80	Singh & Tikoo	1980
	308.15	0.19	2.71	Baabor & Delgado	1991
	308.15–368.15	0.22	6.20	Connaughton et al.	1986
	318.15	1.67	5.42	Hölemann & Kohner	1931
	323.15	0.005	0.98	Millero et al.	1972
NaBr	288.15–328.15	0.05	8.00	Isono	1984
	298.15	1.00	6.03	Kohner	1928
	298.15	0.006	1.03	Geffcken & Price	1934
	298.15	0.06	0.54	Desnoyers et al.	1969
	298.15	0.05	1.80	Vaslow	1969
	298.15	0.03	1.01	Fortier et al.	1974
	298.15	0.10	1.00	Millero et al.	1977
	298.15	0.35	4.36	Karapet'yants et al.	1979
	298.15	0.05	4.97	Gates & Wood	1985
	298.15	1.00	8.34	Grzybkowski & Atkinson	1986
	298.15	0.09	0.41	Kawaizumi et al.	1988
	298.15	0.50	4.00	Kumar	1988a
	298.15–343.15	0.27	6.36	Geffcken	1931
	308.15	1.05	9.39	Scott & Wilson	1934
NaHCO₃	278.15–318.15	0.003	1.01	Hershey et al.	1983
	298.15	0.10	0.80	Millero et al.	1977
Na₂CO₃	278.15–318.15	0.007	1.01	Hershey et al.	1983
	293.15–303.15	0.20	1.84	Palaty	1991
	293.15–333.15	0.31	1.69	Goncalves & Kestin	1981
	298.15	0.09	1.54	Intern. Crit. Tables	1928
	298.15	0.48	2.46	Pesce	1932
	298.15	0.05	1.88	Geffcken & Price	1934
	298.15	0.20	0.90	Millero et al.	1977
Na₂SO₄	288.15–308.15	0.003	0.72	Chen et al.	1980
	288.15–318.15	0.05	1.62	Lo Surdo et al.	1982
	288.15–328.15	0.05	1.50	Isono	1984, 1985
	298.15	0.06	1.96	Trimble	1922
	298.15	0.07	2.22	Intern. Crit. Tables	1928
	298.15	0.5	1.08	Kohner	1928
	298.15	0.004	0.90	Geffcken & Price	1934
	298.15	0.07	2.74	Gibson	1934
	298.15	0.10	1.96	Pearce & Eckstrom	1937
	298.15	0.20	0.84	Dunn	1966
	298.15	0.10	1.00	Millero et al.	1977
	298.15	0.33	1.00	Millero et al.	1985
	298.15–323.15	0.01	0.33	Chen et al.	1977
	298.15–348.15	0.01	0.15	Fabuss et al.	1966
	298.15–348.15	0.05	1.00	Ellis	1968
	298.15–348.15	0.03	1.18	Korosi & Fabuss	1968
	298.15–368.15	0.65	0.65	Dedick et al.	1990
	308.15	0.11	1.92	Singh & Tikoo	1980
	308.15–368.15	0.10	2.07	Connaughton et al.	1986
	313.15–353.15	0.70	9.49	Sohnel et al.	1984
	323.15	0.002	1.00	Millero & Knox	1973
	328.15–368.15	0.94	1.14	Connaughton & Millero	1987
KCl	278.15–368.15	0.005	4.50	Dedick et al.	1990
	288.15–308.15	0.001	0.51	Kaminsky	1957
	288.15–328.15	0.19	0.81	Dunn	1968
	288.15–328.15	0.05	4.00	Isono	1980

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for calculations of volumetric ion interaction parameters at various temperatures—Continued

Solute	Temperature (K)	Concentration		Literature source	Year
		from	to		
	288.15–348.15	0.04	1.00	Out & Los	1980
	293.15–303.15	0.33	4.55	Goncalves & Kestin	1977
	293.15–308.15	0.10	4.69	Lengyel et al.	1964
	293.15–308.15	0.12	0.12	Millero & Drost-Hansen	1968
	298.15	0.002	0.20	Jones & Talley	1933a
	298.15	0.51	3.27	Jones & Talley	1933b
	298.15	0.01	0.82	Geffcken & Price	1934
	298.15	0.17	4.43	Gibson	1934
	298.15	0.55	2.22	Lanman & Mair	1934
	298.15	0.0001	3.31	Jones & Ray	1937
	298.15	0.04	1.03	Wirth	1937
	298.15	0.005	2.00	Halasey	1941
	298.15	0.10	1.37	Drucker	1946
	298.15	0.01	0.60	MacInnes & Dayhoff	1952
	298.15	0.007	0.42	Spedding et al.	1966
	298.15	0.03	2.93	Vaslow	1966
	298.15	0.02	1.00	Fortier et al.	1974
	298.15	0.33	1.00	Chen et al.	1977
	298.15	0.10	1.00	Millero et al.	1977
	298.15	0.05	2.01	Olofsson	1979
	298.15	0.06	3.01	Gates & Wood	1985
	298.15	0.50	4.50	Kumar	1986b, 1988b
	298.15	0.13	0.48	Kawaizumi et al.	1988
	298.15–318.15	0.50	4.50	Romankiw & Chou	1983
	298.15–343.15	0.17	5.36	Geffcken	1931
	298.15–348.15	0.10	3.54	Korosi & Fabuss	1968
	308.15	1.07	4.81	Scott & Wilson	1934
	308.15	0.32	1.74	Singh & Tikoo	1980
	308.15	0.20	2.80	Baabor & Delgado	1991
	308.15–318.15	0.05	4.63	Firth & Tyrrell	1962
	323.15	0.03	1.00	Millero & Knox	1973
KBr	283.15–298.15	0.11	4.54	Lengyel et al.	1964
	293.15–308.15	0.10	0.10	Millero & Drost-Hansen	1968
	293.15–328.15	0.05	4.00	Isono	1984
	298.15	0.001	4.37	Jones & Talley	1933b
	298.15	0.0003	4.38	Jones & Bickford	1934
	298.15	0.04	1.05	Wirth	1937
	298.15	0.05	0.63	Desnoyers et al.	1969
	298.15	0.06	0.98	Fortier et al.	1974
	298.15	0.10	1.00	Millero et al.	1977
	298.15	1.00	4.00	Kumar	1985
	298.15	0.08	0.35	Kawaizumi et al.	1988
	298.15–323.15	0.23	5.57	Geffcken	1931
	298.15–328.15	0.20	0.92	Dunn	1968
	298.15–348.15	0.10	1.00	Ellis	1968
	298.15–368.15	0.05	1.20	Out & Los	1980
	308.15	0.98	5.62	Scott et al.	1934
K₂CO₃	293.15–333.15	0.06	7.62	Goncalves & Kestin	1981
	298.15	0.07	7.24	Intern. Crit. Tables	1928
	298.15	0.30	0.90	Millero et al.	1977
K₂SO₄	288.15–308.15	0.003	0.09	Kaminsky	1957
	288.15–368.15	0.01	0.65	Dedick et al.	1990
	298.15	0.03	0.64	Adams	1932
	298.15	0.0002	0.004	Jones & Ray	1937
	298.15	0.10	0.69	Pearce & Eckstrom	1937
	298.15	0.01	0.33	Wirth	1937
	298.15	0.001	0.51	Jones & Colvin	1940
	298.15	0.21	0.51	Dunn	1966
	298.15	0.10	0.50	Millero et al.	1977
	298.15–348.15	0.05	0.50	Ellis	1968

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for calculations of volumetric ion interaction parameters at vari
temperatures—Continued

| Solute | Temperature (K) | Concentration | | Literature source | Year |
		from	to		
	323.15	0.002	0.71	Millero & Knox	1973
MgCl$_2$	288.15–298.15	0.01	5.28	Lo Surdo *et al.*	1982
	288.15–308.15	0.003	0.16	Kaminsky	1957
	288.15–308.15	0.012	5.94	Berecz & Bader	1973
	288.15–308.15	0.005	1.48	Chen *et al.*	1980
	288.15–318.15	0.05	5.00	Isono	1984
	298.15	0.71	3.03	Herz	1914
	298.15	0.04	0.23	Shedlovsky & Brown	1934
	298.15	0.19	0.70	Dunn	1966
	298.15	0.50	5.11	Vasilev *et al.*	1973
	298.15	0.004	0.34	Perron *et al.*	1974
	298.15	0.009	0.31	Chen *et al.*	1977
	298.15	0.05	0.97	Millero *et al.*	1977
	298.15	0.03	5.67	Phang & Stokes	1980
	298.15	0.03	1.02	Emara & Farid	1981
	298.15	0.14	5.03	Perron *et al.*	1981
	298.15	0.30	5.78	Miller *et al.*	1984
	298.15	0.03	2.95	Gates & Wood	1985
	298.15	0.33	1.00	Millero *et al.*	1985
	298.15	0.17	1.50	Kumar	1989
	298.15–318.15	0.54	3.31	Romankiw & Chou	1983
	298.15–348.15	0.06	6.17	Rutskov	1948
	308.15	0.11	1.95	Singh & Tikoo	1980
	308.15–368.15	0.35	4.48	Connaughton *et al.*	1986
	323.15	0.003	0.99	Millero & Knox	1973
	368.15	1.03	1.05	Connaughton & Millero	1987
MgBr$_2$	283.15–363.15	0.11	4.44	Intern. Crit. Tables	1928
MgSO$_4$	288.15–308.15	0.0005	1.02	Kaminsky	1957
	288.15–308.15	0.001	1.23	Chen *et al.*	1980
	288.15–318.15	0.05	2.40	Lo Surdo *et al.*	1982
	288.15–328.15	0.05	2.50	Isono	1980
	298.15	0.61	2.53	Herz	1914
	298.15	0.02	0.25	Chen *et al.*	1977
	298.15	0.05	1.00	Millero *et al.*	1977
	298.15	0.013	1.01	Emara & Farid	1981
	298.15	0.25	0.75	Millero *et al.*	1985
	298.15–348.15	0.01	0.29	Fabuss *et al.*	1966
	298.15–348.15	0.03	0.89	Korosi & Fabuss	1968
	308.15	0.10	1.39	Singh & Tikoo	1980
	308.15–368.15	0.21	2.84	Connaughton *et al.*	1986
	323.15	0.002	0.89	Millero & Knox	1973
	328.15–368.15	0.72	0.78	Connaughton & Millero	1987
CaCl$_2$	288.15–303.15	1.00	8.00	Jakli *et al.*	1983
	288.15–308.15	0.33	7.44	Kumar & Atkinson	1983
	288.15–328.15	0.22	0.73	Dunn	1968
	288.15–328.15	0.05	6.00	Isono	1984
	298.15	1.29	6.72	Pesce	1932
	298.15	0.04	0.13	Shedlovsky & Brown	1934
	298.15	2.71	7.68	Lyons & Riley	1954
	298.15	0.18	0.79	Dunn	1966
	298.15	0.52	5.68	Vasilev *et al.*	1973
	298.15	0.01	0.33	Perron *et al.*	1974
	298.15	0.01	0.98	Millero *et al.*	1977
	298.15	0.02	0.40	Spitzer *et al.*	1978
	298.15	0.02	0.51	Emara & Farid	1981
	298.15	0.05	6.46	Perron *et al.*	1981
	298.15	0.03	7.40	Kumar *et al.*	1982
	298.15	0.05	0.25	Gates & Wood	1985
	298.15	0.17	1.50	Kumar	1986b
	298.15–303.15	0.05	0.05	Nowicka *et al.*	1988

TABLE 1. Literature sources of experimental densities and apparent molal volumes used for calculations of volumetric ion interaction parameters at various temperatures—Continued

| Solute | Temperature (K) | Concentration | | Literature source | Year |
		from	to		
	298.15–308.15	0.14	6.41	Oakes *et al.*	1990
	298.15–318.15	0.46	5.05	Romankiw & Chou	1983
	298.15–348.15	0.05	11.10	Rutskov	1948
CaBr$_2$	283.15–363.15	0.10	5.00	Intern. Crit. Tables	1928
	298.15	0.40	260	Grzybkowski & Atkinson	1986
SrCl$_2$	293.15–303.15	0.05	2.50	Isono	1984, 1985
	293.15–363.15	0.13	3.40	I.C.T.	1928
	298.15	0.95	3.00	Pesce	1932
	298.15	0.05	0.25	Shedlovsky & Brown	1934
	298.15	0.006	0.61	Kruis	1936
	298.15	0.004	0.33	Perron *et al.*	1974
	298.15	0.20	1.00	Millero *et al.*	1977
SrBr$_2$	293.15–363.15	0.08	3.31	Intern. Crit. Tables	1928
BaCl$_2$	288.15–303.15	1.0	2.0	Jakli *et al.*	1983
	288.15–328.15	0.19	0.83	Dunn	1968
	288.15–328.15	0.05	1.5	Isono	1984
	298.15	0.25	1.47	Kohner	1928
	298.15	0.4	1.52	Geffcken	1931
	298.15	0.54	0.54	Shedlovsky & Brown	1934
	298.15	0.0001	1.00	Jones & Ray	1941
	298.15	0.19	0.75	Dunn	1966
	298.15	0.003	0.39	Perron *et al.*	1974
	298.15	0.1	0.96	Millero *et al.*	1977
	308.15	0.09	1.69	Singh & Tikoo	1980
BaBr$_2$	293.15–363.15	0.07	2.24	Intern. Crit. Tables	1928

3.2. Computation of Temperature Variations of $\bar{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX} Parameters

We will accept the terminology earlier suggested by us [Krumgalz *et al.* (1994)] for the convenience of further discussion. The term "a restricted set of volumetric ion interaction parameters" will be employed to refer to a set including the fixed apparent molal solute volume at an infinite dilution calculated by the additivity rule from apparent ionic molal solute volumes, whereas the term "an unrestricted set of volumetric ion interaction parameters" will be employed to refer to a set including the unfixed apparent molal solute volume computed along with other volumetric ion interaction parameters from experimental data. Connaughton *et al.* (1986) called the volumetric ion interaction parameters appropriate to our unrestricted sets as those found by a "float method," and restricted sets as those found by a "fixed method." We would like to emphasize that we initially conducted simultaneous determinations of $\bar{V}^0_{MX}$ values in unrestricted sets of ion interaction parameters. However, after analyzing the results of unrestricted calculations, we found that $\bar{V}^0_{MX}$ values found by unrestricted calculations for various temperatures could yield a confusing set of results. Thus, another coordinated method was required for $\bar{V}^0_{MX}$ determination, and Millero's (1972a), (1972b) very extensive analysis of $\bar{V}^0_{MX}$ values was certainly useful. Therefore, to be consistent with our 298.15 K article [Krumgalz *et al.* (1994),

(1996)], we used a "restricted" approach in the current article for ion interaction parameters calculations in most cases at temperatures others than 298.15 K. Thus, we recommended that in most cases, the restricted sets of volumetric ion interaction parameters be used at all studied temperatures when the $\bar{V}^0_{MX}$ values could be calculated from the recommended $\bar{V}^0_{ion}$ values by an additivity rule. We have expended great efforts in obtaining the best values of various parameters for 298.15 K, which were published by us recently [Krumgalz *et al.* (1996)], with every implication that they are indeed of "reference data" quality. The experimental data for any other temperature is much more limited. Therefore, there is every reason to retain our 298.15 K values as fixed exactly. Therefore, all recommended volumetric ion interaction parameters at 298.15 K for the above-mentioned solutions are those published by us earlier [Krumgalz *et al.* (1996)]. For the solutions of sodium salts (NaCl, NaBr, Na$_2$SO$_4$) and of chlorides (KCl, MgCl$_2$, CaCl$_2$, SrCl$_2$, BaCl$_2$), the recommended volumetric ion interaction parameters at 298.15 K are unrestricted sets of parameters, and for other solutions, they are restricted ones taken from Krumgalz *et al.* (1996).

The following procedure was used for the calculations of Pitzer's volumetric ion interaction parameters. The calculations of the sets of volumetric ion interaction parameters ($\bar{V}^0_{MX}$, $\beta^{(0)V}_{MX}$, $\beta^{(1)V}_{MX}$, $\beta^{(2)V}_{MX}$, and C^V_{MX}) for various types of single-solute electrolyte solutions were carried out in a

288.15–368.15 K temperature interval by using the most reliable density and apparent molal volume data for single-solute electrolyte solutions available in the literature. The calculations were conducted by the least square method earlier described in detail by Krumgalz *et al.* (1994). The experimental volumetric data for some electrolyte solutions sometimes covered a more limited temperature interval than 288.15–368.15 K. Therefore, the covered temperature interval for each electrolyte was noted in the proper tables. The computations were carried out in a double precision mode using a program created by Professor Ya. Iosilevskii for inverting matrices by the Gauss–Jordan method. The procedure of the calculation and selection of the best volumetric ion interaction parameters at various temperatures consisted of the following steps:

(i)   calculation of volumetric ion interaction parameters $\bar{V}_{MX}^0$, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and C_{MX}^V sets; and

(ii)   detection of poor sets of volumetric ion interaction parameters.

This step was conducted by analyzing the fitting of the calculated ρ and $V_{\phi,MX}$ values obtained by using computed sets of volumetric ion interaction parameters with experimental ρ and $V_{\phi,MX}$ values at various temperatures. Large standard deviations of differences between the experimental and calculated densities $\sigma(\Delta\rho)$ and apparent molal volumes $\sigma(\Delta V_{\phi,MX})$ were observed for some particular cases. It was concluded that the computed volumetric ion interaction parameters for these cases were poor ones.

Special attention was given to the problem of calculating the $\beta_{MX}^{(2)V}$ parameter for 2:2 electrolytes. Earlier, Pitzer and Mayorga (1974) observed the peculiar behavior of activity coefficients of 2:2 valence type electrolytes. This phenomenon was discussed by them in terms of various theories, some of which assume ion pair formation in such solutions while others do not. More than 70 yr ago, Bjerrum (1926) showed that an ionic association could be expected on the basis of purely electrostatic forces for 2:2 electrolytes, even in water. In some cases, the existence of ion pairs in aqueous solutions was proven by spectroscopic or ultrasonic data. Various authors [Pitzer (1972) and references wherein] treated their experimental data for bivalent sulfates by the ion association model. Although this approach fit the data well, there are serious disadvantages that lead one to seek a simpler method. The $\beta_{MX}^{(2)}$ parameter was designed more than 25 yr ago by Pitzer and Mayorga (1974) in order to be able to apply the Pitzer approach to 2:2 aqueous electrolytes characterized by a partial ionic association of M^{2+} and X^{2-} ions. These authors suggested that there were many advantages in representing some thermodynamic properties (activity and osmotic coefficients) of 2:2 electrolytes by including an appropriate virial coefficient containing $\beta_{MX}^{(2)}$ into the Pitzer equation instead of including the parameters determined by a chemical association equilibrium. Such a modified equation has been successfully applied for thermodynamic calculations (ion activity and osmotic coefficients) both for single

2:2 electrolyte solutions and for mixed electrolytes involving even one component of the 2:2 type [Pitzer and Mayorga (1974)]. Gronwall *et al.* (1928), Guggenheim (1959); (1960) Gardner and Glueckauf (1971), and Rasaiah (1972) demonstrated that the experimental data for 2:2 electrolytes could be treated without the assumption of an association equilibrium, provided one avoids the Debye–Hückel approximation of linearization of the exponential item in the Boltzmann distribution. However, the equations now become so complex, that one has only a few numerical results for particular ionic models. Thus, it was desirable to deal with the development of equations that were simpler that those now available, but which still reflect adequately the complexities of actual thermodynamic properties of the solutions. Therefore one of the aims of the current paper was the further development of Pitzer's volumetric ion interaction approach for 2:2 electrolyte solutions.

In our earlier publication [Krumgalz *et al.* (1996)], we demonstrated that there was a mathematical problem in the $\beta_{MX}^{(2)V}$ parameter calculation: there was effective redundancy between the $\bar{V}_{MX}^0$ and $\beta_{MX}^{(2)V}$ parameters at solution concentrations larger than ~ 0.15 mol·(kg solvent)$^{-1}$. Therefore, reliable values of $\beta_{MX}^{(2)V}$ can be counted only for diluted solution for which precise density data for the solutions with concentrations of less than 0.15 mol·(kg solvent)$^{-1}$ are available. For almost all 2:2 electrolytes, reliable density data for very diluted solutions at various temperatures are missing, with the exception of $MgSO_4$ solutions. Therefore, at the present situation the $\beta_{MX}^{(2)V}$ parameters could be calculated only for $MgSO_4$ solutions amongst all 2:2 electrolytes.

Some aspects of the calculation of the C_{MX}^V term should also be clarified. In our earlier papers [Krumgalz *et al.* (1994), (1996)] we recommended that this term be omitted when density data does not exceed 0.7 mol·(kg H_2O)$^-$. Among all the data discussed, only those of K_2SO_4 at 288.15 and 348.15 K do not exceed a molality equal to 0.7 mol·(kg H_2O)$^{-1}$. However, in our earlier publication [Krumgalz *et al.* (1994); (1996)], we recommended the C_{MX}^V term for K_2SO_4 at 298.15 K. Therefore, in order to be consistent with earlier publications, we decided to calculate the C_{MX}^V term for K_2SO_4 at temperatures other than 298.15 even for concentration levels less than 0.7 mol·(kg H_2O)$^{-1}$.

Reliability of volumetric ion interaction parameters obtained as described above can be checked by their ability to fit experimental data with relatively small errors. The checking procedure consisted of using obtained sets of volumetric ion interaction parameters for back computation of apparent molal volumes of solutes and densities of single-solute electrolyte solutions by Eqs. (1) and (2) for the entire range of concentrations in which experimental data were available. The analysis of arithmetical means of the differences between the experimental and calculated values of the solution densities, $(\Delta\rho)_{av} = (\rho_{exp} - \rho_{calc})_{av}$ together with their standard deviations $\sigma(\Delta\rho)$ allows us to discard poor sets of volumetric ion interaction parameters. We considered the sets of volumetric ion interaction parameters yielding $\sigma(\Delta\rho) > 0.001$ g cm^{-3} as poor sets. As it was found, none of the

TABLE 2. Temperature dependence of $\bar{V}^0_{MX}$ values: $\bar{V}^0_{MX}=A_0+A_1\cdot(T-298.15)+A_2\cdot(T-298.15)^2+A_3\cdot(T-298.15)^3+A_4\cdot(T-298.15)^4+A_5\cdot(T-298.15)^5$

Salt	Temperature (K)	A_0	$A_1\cdot10^2$	$A_2\cdot10^3$	$A_3\cdot10^5$	$A_4\cdot10^7$	$A_5\cdot10^9$
NaCl	278.15–368.15	16.620	8.7385	−1.9994	1.7452	−0.8023	
NaBr	288.15–328.15	23.479	10.495	−2.2351	4.7513	−6.4325	
NaHCO$_3$[a]	278.15–318.15	23.181	11.309	−5.5413	2.0591		
Na$_2$SO$_4$	288.15–368.15	11.776	22.858	−4.2216	1.7764		
Na$_2$CO$_3$[a]	288.15–333.15	−6.480	25.109	−6.8782	5.4186		
KCl	288.15–368.15	26.848	7.2395	−2.0757	1.930	−0.9716	
KBr	283.15–328.15	33.710	9.4338	−1.6027			
KHCO$_3$[b]	278.15–318.15	33.833	9.740	−6.7132	1.850		
K$_2$SO$_4$	288.15–368.15	32.230	19.445	−4.1171	1.9525	−0.4683	
K$_2$CO$_3$[a]	293.15–333.15	14.129	15.648	1.8059	−11.838		
MgCl$_2$	288.15–368.15	14.083	7.4817	0.28395	−7.7096	6.4510	
MgBr$_2$	283.15–363.15	27.800	12.460	−0.3829	−6.0871	5.5808	
Mg(HCO$_3$)$_2$[c]	278.15–318.15	28.563	12.66	−11.99	1.633		
MgSO$_4$	288.15–368.15	−7.380	14.065	−2.7682			
MgCO$_3$[c]	278.15–333.15	−25.247	14.65	2.518	3.147	−3.029	
CaCl$_2$	288.15–328.15	17.612	5.2384	−1.6573	−0.7341		
CaBr$_2$	283.15–363.15	31.33	9.2147	−2.0952	1.8924	−2.2264	0.7033
Ca(HCO$_3$)$_2$[c]	278.15–318.15	31.840	9.585	−13.24	8.550		
CaSO$_4$[c]	288.15–368.15	−3.694	10.347	−3.1047	2.4273	−1.9620	
CaCO$_3$[c]	278.15–333.15	−21.970	11.57	−3.422	3.741	−12.19	
SrCl$_2$	293.15–363.15	17.691	7.6489	−1.5221			
SrBr$_2$	293.15–363.15	31.452	11.393	−1.3727			
Sr(HCO$_3$)$_2$[c]	278.15–318.15	31.431	14.45	−12.76	6.342		
SrSO$_4$[c]	288.15–368.15	−4.103	14.796	−2.6437	1.0199	−0.8814	
SrCO$_3$[c]	278.15–333.15	−22.379	16.44	−3.065	1.549	−9.167	
BaCl$_2$	288.15–328.15	22.975	21.185	−1.0572	−13.483	26.772	
BaBr$_2$	293.15–363.15	36.70	23.299	−0.6239	−5.4314	4.4277	
Ba(HCO$_3$)$_2$[c]	278.15–318.15	37.109	24.83	−11.63	−0.2833		
BaSO$_4$[c]	288.15–368.15	1.575	24.411	−1.6095	−4.1351	3.0134	
BaCO$_3$[c]	278.15–333.15	−16.701	26.82	−2.216	−5.065	−1.696	

[a] $\bar{V}^0_{MX}$ values for NaHCO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$ are from our unrestricted sets of volumetric ion interaction parameters for these solutions presented in Table 3.

[b] $\bar{V}^0_{KHCO_3}$ values were calculated by the additivity rule by using temperature dependency of the $\bar{V}^0_{HCO_3^-}$ value discussed later in this article (Table 9).

[c] $\bar{V}^0_{MX}$ values for poor soluble salts were calculated by using our $\bar{V}^0_M$ and $\bar{V}^0_X$ values at 298.15 K and those of Millero (1972a) (1972b) at other temperatures. $\bar{V}^0_{HCO_3^-}$ and $\bar{V}^0_{CO_3^{2-}}$ values used for calculations at temperatures other than 298.15 K are discussed later in this article (Table 9).

volumetric ion interaction parameters at various temperatures could be considered as poor sets.

Let us consider the calculations of restricted sets of volumetric ion interaction parameters in detail. Such calculations require the knowledge of the $\bar{V}^0_{M_{\nu_M}X_{\nu_X}}$ value for electrolyte $M_{\nu_M}X_{\nu_X}$ at various temperatures determined by the additivity rule

$$\bar{V}^0_{M_{\nu_M}X_{\nu_X}}=\nu_M\cdot\bar{V}^0_M+\nu_X\cdot\bar{V}^0_X, \qquad (18)$$

where $\bar{V}^0_M$ and $\bar{V}^0_X$ are the partial ionic volumes of a cation and an anion, respectively, at infinite dilution. In our calculation procedure, we used $\bar{V}^0_M$ and $\bar{V}^0_X$ values taken from Millero (1972a) at all temperatures in an interval 273.15–473.15 K (where it was possible), except his values at 298.15 K, which were replaced for our $\bar{V}^0_M$ and $\bar{V}^0_X$ values at 298.15 K [Krumgalz et al. (1996)]. For convenience of the calculations, $\bar{V}^0_M$ and $\bar{V}^0_X$ values have been described by a polyno-

mial expression relative to temperature. We then calculated the ionic $\bar{V}^0_M$ and $\bar{V}^0_X$ values with a 5 K step. Using these calculated ionic values, we calculated the $\bar{V}^0_{MX}$ values for each electrolyte of interest by the additivity rule expressed by Eq. (18). The $\bar{V}^0_{MX}$ values obtained with the 5 K steps were used for calculating coefficients for polynomial dependence of apparent molal volume of each electrolyte at an infinite dilution in the form of $\bar{V}^0_{MX}=\Sigma_0^n A_i\cdot(T-298.15)^i$. The polynomial equation of the 5th degree maximum expressed by Eq. (19) for description of the function $\bar{V}^0_{MX}$ was chosen since such an equation yields very sound precision

$$\bar{V}^0_{MX}=A_0+A_1\cdot(T-298.15)+A_2\cdot(T-298.15)^2$$
$$+A_3\cdot(T-298.15)^3+A_4\cdot(T-298.15)^4$$
$$+A_5\cdot(T-298.15)^5, \qquad (19)$$

where $A_0=\bar{V}^0_{MX}$ at 298.15 K. The coefficients of this func-

TABLE 3. The unrestricted volumetric ion interaction parameters recommended for volumetric calculations at various temperatures for $NaHCO_3$, Na_2CO_3, and K_2CO_3 solutions

Solute	Temperature (K)	$\bar{V}^0_{MX}$	$\beta^{(0)V}_{MX} \cdot 10^5$	$\beta^{(1)V}_{MX} \cdot 10^5$	$C^V_{MX} \cdot 10^6$	m_{max}
$NaHCO_3$	278.15	18.51	−12.658	57.074	50.780	1.0
	288.15	21.59	−11.318	45.031	37.815	1.0
	298.15[a]	23.181	−1.1620	17.80		1.0
	308.15	23.90	−6.5235	30.219	19.610	1.0
	318.15	23.36	−29.378	86.739	96.470	1.0
Na_2CO_3	288.15	−9.72	6.7256	17.426	−3.2798	1.0
	293.15	−7.89	6.4042	14.259	−3.8615	1.7
	298.15[a]	−6.48	5.9800	8.1600	−3.2500	1.7
	303.15	−5.28	6.0349	2.8284	−4.0224	1.7
	313.15	−4.04	5.2776	−0.2333	−3.3888	1.7
	318.15	−3.83	4.4268	1.7129	−2.1864	1.0
	323.15	−3.66	4.2369	1.2027	−2.1884	1.7
	333.15	−3.79	3.9187	0.0574	−2.0928	1.7
K_2CO_3	293.15	13.57	4.2102	10.431	−1.1413	7.6
	298.15	14.13	3.4930	16.511	−0.8468	7.6
	303.15	15.31	3.6820	5.1411	−0.9678	7.6
	313.15	16.43	3.2657	0.8369	−0.8315	7.6
	323.15	17.29	3.0007	−5.4478	−0.7535	7.6
	333.15	16.76	2.6803	−4.1785	−0.6437	7.6

[a]These volumetric ion interaction parameters at 298.15 K were taken from Monnin (1989).

tion for various electrolyte solutions have been statistically approximated by the least square method and presented in Table 2. The temperature interval for each salt corresponded to the temperature interval of density measurements if it was less than $288.15 \div 368.15$ K. The additional explanation related to the $\bar{V}^0_{MX}$ value calculations should be given in cases of poor soluble electrolytes such as $Mg(HCO_3)_2$, $MgCO_3$, $Ca(HCO_3)_2$, $CaCO_3$, $CaSO_4$, $Sr(HCO_3)_2$, $SrCO_3$, $SrSO_4$, $Ba(HCO_3)_2$, $BaCO_3$, and $BaSO_4$. Reliable density data for these electrolytes were missing at various temperatures due to poor solubility of these electrolytes. Therefore, we could not calculate the complete sets of volumetric ion interaction parameters for these electrolytes at various temperatures. Only temperature dependence of the $\bar{V}^0_{MX}$ values for some of these salts could be calculated by using our $\bar{V}^0_M$ and $\bar{V}^0_X$ values at 298.15 K and those of Millero (1972a), (1972b) at other temperatures. The procedure of the calculation of the $\bar{V}^0_{HCO_3^-}$ and $\bar{V}^0_{CO_3^{2-}}$ values at temperatures other than 298.15 K will be discussed later in this paper.

The above mentioned calculation procedure for the $\bar{V}^0_{MX}$ calculation by the additivity rule was used for all electrolytes with the exception of those containing bicarbonates and carbonates anions for which $\bar{V}^0_{HCO_3^-}$ and $\bar{V}^0_{CO_3^{2-}}$ values at temperatures other than 298.15 K were missing in Millero's (1972a) review. Since $\bar{V}^0_{HCO_3^-}$ and $\bar{V}^0_{CO_3^{2-}}$ values at various temperatures have not yet been determined, $\bar{V}^0_{MX}$ values for bicarbonates and carbonates could not be calculated by the additivity rule. Therefore, the restricted volumetric ion interaction parameters for bicarbonate and carbonate salts could also not be determined. In this situation, we suggested that the $\bar{V}^0_{MX}$ values for $NaHCO_3$, Na_2CO_3, and K_2CO_3 solutions from the unrestricted sets of volumetric ion interaction pa-

rameters for these solutions, presented in Table 3, should be used for volumetric calculations at various temperatures.

Calculations of the volumetric ion interaction parameters for each electrolyte were based on experimental density data at various temperatures from different literature sources. In order to be able to use the parameters obtained at any temperature for multiple-solute electrolyte solutions, the temperature dependence of each parameter was expressed in polynomial form with $(T-298.15)$ as a variable. Higher statistical weight was given to values of the parameters at 298.15 K in the least-square evaluation of equation coefficients. There are two exceptional systems: solutions of $SrCl_2$ and $SrBr_2$. Since known values of the densities of both systems are poor quality at all temperatures, the identical statistical weight was assigned to all determinations. The results were presented as the following equations:

$$\beta^{(0)V}_{MX} = B_0 + B_1 \cdot (T-298.15) + B_2 \cdot (T-298.15)^2$$
$$+ B_3 \cdot (T-298.15)^3 + B_4 \cdot (T-298.15)^4$$
$$+ B_5 \cdot (T-298.15)^5, \tag{20}$$

$$\beta^{(1)V}_{MX} = C_0 + C_1 \cdot (T-298.15) + C_2 \cdot (T-298.15)^2$$
$$+ C_3 \cdot (T-298.15)^3 + C_4 \cdot (T-298.15)^4$$
$$+ C_5 \cdot (T-298.15)^5, \tag{21}$$

$$\beta^{(2)V}_{MX} = D_0 + D_1 \cdot (T-298.15) + D_2 \cdot (T-298.15)^2$$
$$+ D_3 \cdot (T-298.15)^3 + D_4 \cdot (T-298.15)^4$$
$$+ D_5 \cdot (T-298.15)^5, \tag{22}$$

TABLE 4. Temperature dependence of $\beta_{MX}^{(0)V}$ values: $\beta_{MX}^{(0)V} = B_0 + B_1 \cdot (T - 298.15) + B_2 \cdot (T - 298.15)^2 + B_3 \cdot (T - 298.15)^3 + B_4 \cdot (T - 298.15)^4 + B_5 \cdot (T - 298.15)^5$

Salt	Temperature (K)	$B_0 \cdot 10^5$	$B_1 \cdot 10^7$	$B_2 \cdot 10^9$	$B_3 \cdot 10^{10}$	$B_4 \cdot 10^{11}$	$B_5 \cdot 10^{13}$
NaCl	278.15–368.15	1.2335	−2.7445	2.4624	−0.0108		
NaBr	288.15–328.15	0.7607	−2.0616	23.746	−6.4078		
NaHCO$_3$	278.15–318.15	−1.1620	−28.646	512.84			
Na$_2$SO$_4$	288.15–368.15	5.3250	−10.930	55.828	−4.6248		
Na$_2$CO$_3$	288.15–333.15	5.9800	−6.9018	2.1120			
KCl	288.15–368.15	1.2793	−1.8784	−1.2365	−0.2720		
KBr	283.15–328.15	1.0660	−3.9576	5.7835			
KHCO$_3$	298.15	−7.241					
K$_2$SO$_4$	288.15–368.15	1.1054	82.980	−263.93	18.459		
K$_2$CO$_3$	293.15–333.15	3.4930	−6.7348	44.902	−9.3417		
MgCl$_2$	288.15–368.15	1.6933	−0.4605	5.7990	−0.7328		
MgBr$_2$	283.15–363.15	−0.0468	3.9927	10.053	−5.1034	0.4181	
MgSO$_4$	288.15–368.15	4.9809	−4.2924	0.3413			
CaCl$_2$	288.15–328.15	1.3107	−2.2290	16.253	−4.3892		
CaBr$_2$	283.15–363.15	2.1496	−4.9548	19.443	−0.2602	−0.6271	0.5196
SrCl$_2$	293.15–363.15	2.8713	−6.2300	5.9853			
SrBr$_2$	293.15–363.15	0.6173	−5.1228	7.7418			
BaCl$_2$	288.15–328.15	0.1921	5.8271	165.53	28.718	−22.268	
BaBr$_2$	293.15–363.15	−12.160	12.704	51.828	−12.361	0.7303	

$$C_{MX}^V = E_0 + E_1 \cdot (T - 298.15) + E_2 \cdot (T - 298.15)^2$$
$$+ E_3 \cdot (T - 298.15)^3 + E_4 \cdot (T - 298.15)^4$$
$$+ E_5 \cdot (T - 298.15)^5, \tag{23}$$

where $B_0 = \beta_{MX}^{(0)V}$, $C_0 = \beta_{MX}^{(1)V}$, $D_0 = \beta_{MX}^{(2)V}$, $E_0 = C_{MX}^V$ are the appropriate values at 298.15 K recently published in Krumgalz et al. (1996). The coefficients A_i, B_i, C_i, D_i, and E_i calculated by the least-square method are presented in Tables 2, and 4–7.

Comparison of $\bar{V}_{MX}^0$ values, calculated by Eq. (19) by using coefficients A_i from Table 2 at various temperatures,

with those calculated by the additivity rule ($\bar{V}_{MX}^0 = \Sigma \bar{V}_{ion,Millero}^0$) demonstrated that there were differences between them in some cases. Therefore, $\beta_{MX}^{(i)V}$ and C_{MX}^V parameters from the restricted sets should be re-evaluated for smoothed $\bar{V}_{MX}^0$ values and then these new $\beta_{MX}^{(i)V}$ and C_{MX}^V parameters would be fit to yield the entries in Tables 2, and 4–7. We doubt that this procedure would be a significant improvement. In order to prove these doubts, we conducted test calculations for NaBr solutions (Table 8). As one can see from this table, the results obtained by using nonsmoothed and smoothed $\bar{V}_{NaBr}^0$ values are identical. Therefore, we sug-

TABLE 5. Temperature dependence of $\beta_{MX}^{(1)V}$ values: $\beta_{MX}^{(1)V} = C_0 + C_1 \cdot (T - 298.15) + C_2 \cdot (T - 298.15)^2 + C_3 \cdot (T - 298.15)^3 + C_4 \cdot (T - 298.15)^4 + C_5 \cdot (T - 298.15)^5$

Salt	Temperature (K)	$C_0 \cdot 10^5$	$C_1 \cdot 10^6$	$C_2 \cdot 10^7$	$C_3 \cdot 10^8$	$C_4 \cdot 10^{10}$	$C_5 \cdot 10^{12}$
NaCl	278.15–368.15	0.4354	−0.9259	0.2980	−0.0327		
NaBr	288.15–328.15	0.9525	−1.4858	−0.8325	0.2693		
NaHCO$_3$	278.15–318.15	17.800	4.4518	13.897			
Na$_2$SO$_4$	288.15–368.15	12.932	−5.1406	−1.3311	0.1552		
Na$_2$CO$_3$	288.15–333.15	8.1600	−7.4232	1.5774			
KCl	288.15–368.15	0.8948	−1.0948	0.5473	−0.0300		
KBr	283.15–328.15	0.8337	−0.4863	0.0491			
KHCO$_3$	298.15	24.275					
K$_2$SO$_4$	288.15–368.15	26.016	−28.743	7.6066	−0.4988		
K$_2$CO$_3$	293.15–333.15	16.511	−2.0346	−8.2554	2.0615		
MgCl$_2$	288.15–368.15	−5.2068	−6.3193	−0.4094	0.1001		
MgBr$_2$	283.15–363.15	14.569	−11.373	−1.3685	0.7532	−0.6438	
MgSO$_4$	288.15–368.15	14.491	−8.3021	0.5385			
CaCl$_2$	288.15–328.15	−2.4575	−0.8388	−1.7754	0.5152		
CaBr$_2$	283.15–363.15	−5.2328	0.5886	−1.5986	−0.0338	0.6086	−0.4538
SrCl$_2$	293.15–363.15	−11.554	−2.2532	−0.0746			
SrBr$_2$	293.15–363.15	24.446	−1.1180	−0.6505			
BaCl$_2$	288.15–328.15	6.7563	−17.334	−4.9337	1.7005		
BaBr$_2$	293.15–363.15	97.186	−17.150	−3.2040	0.9258	−0.5914	

TABLE 6. Temperature dependence of $\beta_{MX}^{(2)V}$ values: $\beta_{MX}^{(2)V} = D_0 + D_1 \cdot (T - 298.15) + D_2 \cdot (T - 298.15)^2 + D_3 \cdot (T - 298.15)^3 + D_4 \cdot (T - 298.15)^4 + D_5 \cdot (T - 298.15)^5$

Salt	Temperature (K)	$D_0 \cdot 10^2$	$D_1 \cdot 10^4$	$D_2 \cdot 10^5$
MgSO$_4$	288.15÷368.15	1.4346	−2.4604	0.1125

TABLE 7. Temperature dependence of C_{MX}^V values: $C_{MX}^V = E_0 + E_1 \cdot (T - 298.15) + E_2 \cdot (T - 298.15)^2 + E_3 \cdot (T - 298.15)^3 + E_4 \cdot (T - 298.15)^4 + E_5 \cdot (T - 298.15)^5$

Salt	Temperature (K)	$E_0 \cdot 10^6$	$E_1 \cdot 10^8$	$E_2 \cdot 10^9$	$E_3 \cdot 10^{10}$	$E_4 \cdot 10^{11}$	$E_5 \cdot 10^{13}$
NaCl	278.15–368.15	−0.6578	1.5101	−0.0055	−0.0016		
NáBr	288.15–328.15	−0.3491	0.9052	−1.8543	0.5436		
NaHCO$_3$	278.15–318.15	13.741	73.175	149.71			
Na$_2$SO$_4$	288.15–368.15	−2.9140	10.798	−9.5282	0.7375		
Na$_2$CO$_3$	288.15–333.15	−3.2500	1.6502	0.6157			
KCl	288.15–368.15	−0.7131	0.6042	0.6737	−0.0952	0.0119	
KBr	283.15–328.15	−0.7017	4.2347	−0.5150			
KHCO$_3$	298.15	39.791					
K$_2$SO$_4$	288.15–368.15	16.192	−432.94	135.95	−10.219		
K$_2$CO$_3$	293.15–333.15	−0.8468	2.4085	−1.9939	0.4258		
MgCl$_2$	288.15–368.15	−0.5698	−0.5530	−0.3070	0.0474		
MgBr$_2$	283.15–363.15	1.0696	−4.7426	−0.7402	0.4480	−0.0381	
MgSO$_4$	288.15–368.15	0.3969	−2.3555	0.2738			
CaCl$_2$	288.15–328.15	−0.1265	1.1014	−0.8674	0.2471		
CaBr$_2$	283.15–363.15	−0.8976	2.5635	−1.2525	−0.0417	0.0603	−0.0488
SrCl$_2$	293.15–363.15	−1.2320	5.5328	−0.5452			
SrBr$_2$	293.15–363.15	0.0502	3.5328	−0.6735			
BaCl$_2$	288.15–328.15	4.9819	−11.895	−39.349	0.0601	3.1635	
BaBr$_2$	293.15–363.15	20.766	−22.341	−7.5102	1.9275	−0.1205	

TABLE 8. Comparison of the influence of the use of nonsmoothed and smoothed $\bar{V}_{NaBr}^0$ values on the precision of the calculations of $(\Delta\rho)_{av}$ and $(\Delta V_\phi)_{av}$ values

	$\{(\Delta\rho)_{av} \pm std\} \cdot 10^6$ (g·cm^{-3})		$(\Delta V_\phi)_{av} \pm std$ (cm^3·mol^{-1})	
Temperature (K)	Calculations with nonsmoothed $\bar{V}_{NaBr}^0$ values	Calculations with smoothed $\bar{V}_{NaBr}^0$ values	Calculations with nonsmoothed $\bar{V}_{NaBr}^0$ values	Calculations with smoothed $\bar{V}_{NaBr}^0$ values
288.15	14±222	14±219	−0.04±0.17	−0.04±0.16
308.15	8±170	8±167	−0.04±0.16	−0.04±0.16
318.15	6±240	6±243	−0.04±0.17	−0.04±0.17
328.15	−1±133	−1±134	0.01±0.06	0.01±0.06

TABLE 9. Partial molal volumes (cm^3·mole^{-1}) of HCO$_3^-$ and CO$_3^{2-}$ anions obtained by polynomial approximation at various temperatures

Ions	278.15	288.15	293.15	298.15		303.15	308.15	313.15	318.15	323.15	333.15
				Temperature (K)							
HCO$_3^-$	21.64	23.72		24.43	24.38$_5$[a]		24.73		24.24		
CO$_3^{2-}$			−6.00±0.11	−4.00±0.01	−4.07$_2$[a]	−4.88±0.12		−4.36±0.07		−4.22±0.34	−4.56

[a]These $\bar{V}_{ion}^0$ values are those from Krumgalz *et al.* (1996) determined from precise experimental density data at 25 °C and they are recommended for all calculations at this temperature.

gest leaving Tables 2, and 4–7 as they are in the paper.

We would like to emphasize that density measurements at 25 °C for each electrolyte are the most precise ones. Therefore, ion interaction parameters calculated from density data at temperatures other than 25 °C are not as precise. Thus, Eqs. (19)–(23) have been calculated by giving a much higher statistical weight to parameters at 298.15 K than those at other temperatures, with the exception of $SrCl_2$ and $SrBr_2$ solutions, as we mentioned above. Nevertheless, parameters $\bar{V}^0_{MX}$, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^V_{MX} at 298.15 K counted from the temperature polynomial expression [Eqs. (19)–(23)] differ from those determined directly from experimental density data at 298.15 K [Krumgalz et al. (1996)]. Therefore, we suggest for the volumetric calculations at 298.15 K to use our reference $\bar{V}^0_{MX}$, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^V_{MX} parameters at 298.15 K from our review paper [Krumgalz et al. (1996)] instead of parameters found at this temperature from temperature polynomial fitting less precise parameters at various temperatures. Equations (19)–(23) are recommended to be used for calculations of volumetric ion interaction parameters at temperatures other than 298.15 K.

For some electrolytes formed by the above mentioned ions, the temperature dependencies of the volumetric ion interaction parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^V_{MX} could not be calculated either due to the lack of experimental density data at present (i.e., $KHCO_3$), or to the poor solubility of these electrolytes [i.e., $Mg(HCO_3)_2$, $MgCO_3$, $Ca(HCO_3)_2$, $CaCO_3$, $CaSO_4$, $Sr(HCO_3)_2$, $SrCO_3$, $SrSO_4$, $Ba(HCO_3)_2$, $BaCO_3$, and $BaSO_4$]. In cases of volumetric calculations for mixed electrolyte solutions containing such electrolytes, we suggest the use of volumetric ion interaction parameters for these electrolytes at 298.15 K at other temperatures also. This suggestion is based on the assumption that the increment of temperature dependencies of these parameters will be negligible for the volumetric calculations of mixed electrolyte solutions, since concentrations of these electrolytes are small in the solutions discussed. If, in rare cases, their concentrations are high, i.e., in cases of highly concentrated solutions containing $KHCO_3$, temperature dependence for the density of complex solutions containing such electrolytes cannot be estimated by the approach developed in the current paper due to the lack of the volumetric ion interaction parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^V_{MX} for this electrolyte at various temperatures.

4. Apparent Molal Ionic Volumes at Infinite Dilution at Various Temperatures

The Pitzer equations for the calculation of volumetric parameters (apparent molal volumes and density) of single electrolyte solutions do not require the knowledge of single-ion apparent molal volumes at infinite dilution. However, as we showed in our earlier publication [Krumgalz et al. (1995)], *the density calculations for multiple-solute electrolyte solutions do require the knowledge of single-ion limiting partial molal volumes*

$$\rho_{mix} = \frac{1000 + \Sigma_{ion} m_{ion} \cdot M_{ion}}{\dfrac{1000}{\rho_0} + \Sigma_{ion} m_{ion} \cdot \bar{V}^0_{ion} + V^{ex}_{mix}}, \qquad (24)$$

where ρ_{mix} is the density of a multiple-solute electrolyte solution, $\bar{V}^0_{ion}$ is the single-ion limiting partial molal volume, and V^{ex}_{mix} is the excess molal volume of a mixed solution calculated by Pitzer's approach. The calculations of single-ion volumes require some extra-thermodynamic assumptions that will be discussed below. The apparent limiting molal single-ion volumes make a dominant contribution to the calculations of the mass density of complex electrolyte solutions calculated by Pitzer's approach. Several detailed surveys discussing methods of calculation of limiting apparent molal volumes and splitting those volumes into ionic contributions have recently been published [Millero (1972a), (1972b); Krumgalz (1980), (1982)]. These methods used the apparent solute molal volumes at an infinite dilution calculated either by Masson (1929), or by Redlich–Meyer [Redlich (1963); Redlich and Meyer (1964)] or by Owen–Brinkley (1949) equations. Values of apparent limiting ionic molal volumes based on an approach that $\bar{V}^0_{H^+} = 0 \ cm^3 \cdot mol^{-1}$ [Millero (1972a)] were used at various temperatures for our further calculations. In our earlier publications [Krumgalz et al. (1994), (1996)] dealing with this problem at 298.15 K, we chose the $\bar{V}^0_{Cl^-}$ and $\bar{V}^0_{Na^+}$ values as basic values for the calculations of other apparent limiting ionic molal volumes. However, since $\bar{V}^0_{HCl}$ values could be calculated only in a very limited temperature interval, we decided to use apparent ionic limiting molal volumes presented in Millero (1972a) as basic values for the separation of apparent limiting molal volumes into ionic contributions. In addition to Millero's apparent limiting ionic molal volumes, we calculated some new ones ($\bar{V}^0_{HCO_3^-}$ and $\bar{V}^0_{CO_3^{2-}}$) missing in Millero's review (1972a), using the $\bar{V}^0_{MX}$ values from sets of unrestricted volumetric ion interaction parameters for $NaHCO_3$, Na_2CO_3, and K_2CO_3 solutions presented in Table 3. The temperature dependence of the estimated apparent limiting ionic molal volumes of HCO_3^- and CO_3^{2-} anions is presented in Table 9.

5. Density Calculations for Multiple-Solute Electrolyte Solutions at Various Temperatures

The purpose of our paper was to develop the use of the Pitzer volumetric ion interaction parameters for volumetric calculations applied to natural waters and complex industrial solutions at temperature intervals existing in their specific conditions. Since our sets of volumetric ion interaction parameters were obtained by the same procedure, they are self-consistent. Therefore, we recommend using them in calculating volumetric properties of complex electrolyte solutions and natural brines at various temperatures where temperature ranges are determined by the availability of precise experi-

TABLE 10. Comparison of density calculations precision for multiple solute electrolyte solutions $Na^+ + K^+ + Mg^{2+} + Ca^{2+} + Cl^- + H_2O$ at various temperatures

| Solution concentration, mol·(kg H$_2$O)$^{-1}$ | | | | | Ionic strength | Differences between experimental and calculated densities (g cm^{-3}) at various temperatures | | | | |
Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$		293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1.8453	0.1831	1.6380	0.4502	6.2048	8.2930	0.000 220		0.000 066		0.000 118
1.8453	0.1831	2.0133	0.4502	6.9554	9.4189	0.000 164		0.000 022		0.000 150
1.8453	0.1831	1.6380	0.4802	6.2648	8.3830	0.000 220		0.000 092		0.000 119
1.8453	0.1831	2.0133	0.4802	7.0154	9.5089	0.000 204		0.000 048		0.000 176
1.8994	0.1831	1.6380	0.4502	6.2589	8.3471	0.000 196		0.000 066		0.000 082
1.8994	0.1831	2.0133	0.4502	7.0095	9.4730	0.000 248		0.000 108		0.000 182
1.8994	0.1831	1.6380	0.4802	6.3189	8.4371	0.000 209		0.000 067		0.000 105
1.8994	0.1831	2.0133	0.4802	7.0695	9.5630	0.000 253		0.000 089		0.000 199
1.8453	0.2200	1.6380	0.4502	6.2417	8.3299	0.000 189		0.000 029		0.000 070
1.8453	0.2200	2.0133	0.4502	6.9923	9.4558	0.000 218		0.000 047		0.000 163
1.8453	0.2200	1.6380	0.4802	6.3017	8.4199	0.000 191		0.000 061		0.000 088
1.8453	0.2200	2.0133	0.4802	7.0523	9.5458	0.000 215		0.000 035		0.000 163
1.8994	0.2200	1.6380	0.4502	6.2958	8.3840	0.000 191		0.000 045		0.000 073
1.8994	0.2200	2.0133	0.4502	7.0464	9.5099	0.000 187		0.000 016		0.000 129
1.8994	0.2200	1.6380	0.4802	6.3558	8.4740	0.000 218		0.000 091		0.000 108
1.8994	0.2200	2.0133	0.4802	7.1064	9.5999	0.000 223		0.000 085		0.000 200
1.8724	0.2016	1.9195	0.4652	6.8434	9.2281		0.000 180	0.000 019	0.000 126	
1.8724	0.2016	1.7319	0.4652	6.4682	8.6653		0.000 245	0.000 090	0.000 172	
1.8724	0.2016	1.8257	0.4727	6.6708	8.9692		0.000 184	0.000 041	0.000 137	
1.8724	0.2016	1.8257	0.4577	6.6408	8.9242		0.000 248	0.000 103	0.000 189	
1.8859	0.2016	1.8257	0.4652	6.6693	8.9602		0.000 248	0.000 081	0.000 185	
1.8589	0.2016	1.8257	0.4652	6.6423	8.9332		0.000 238	0.000 085	0.000 184	
1.8724	0.2108	1.8257	0.4652	6.6650	8.9559		0.000 297	0.000 138	0.000 216	
1.8724	0.1923	1.8257	0.4652	6.6465	8.9374		0.000 185	0.000 027	0.000 143	
1.8724	0.2016	1.8257	0.4652	6.6558	8.9467		0.000 237	0.000 097	0.000 174	
$\Delta\rho_{av} = (\rho_{exp} - \rho_{calc})_{av}$ [a]						0.000 209	0.000 229	0.000 066	0.000 169	0.000 133
$\sigma(\rho_{exp} - \rho_{calc})$ [b]						0.000 023	0.000 039	0.000 032	0.000 029	0.000 044

[a] $\Delta\rho_{av} = (\rho_{exp} - \rho_{calc})_{av}$ is the average difference between experimental and calculated densities for a proper temperature.

[b] $\sigma(\rho_{exp} - \rho_{calc})$ is the standard deviation of the differences between the experimental and calculated densities for a proper temperature.

mental data. The above sets of volumetric ion interaction parameters should be checked for their reliability with regard to density calculations of mixed solutions. Let us consider a particular case: the Dead Sea waters. The temperatures of these waters has never dropped below 286 K. Therefore, the low temperature level for our calculations was chosen higher than 283 K. We do not recommend extrapolating the recommended equations below 283 K or above the high level temperature presented in Tables 2, and 4–7.

In order to demonstrate reliability of the volumetric ion interaction parameters obtained at various temperatures, we have used them to calculate the density of very concentrated $NaCl + KCl + MgCl_2 + CaCl_2 + H_2O$ solutions resembling the Dead Sea waters. Table 10 presents a comparison of the results so obtained with the experimental data of Krumgalz and Millero (1982). As can be seen from this table, the calculated values and experimental results are in fair agreement. Therefore, we are quite confident in presenting the new sets of Pitzer's parameters at various temperatures for the selected, above mentioned electrolytes. It is understood that as new precise experimental volumetric data (density and apparent molal volumes) of the discussed electrolytes become available, the volumetric ion interaction parameters proposed should be updated for these electrolytes.

We would like to point out here that, as seen from the results presented in Table 10, the calculated densities of multiple electrolyte solutions are smaller than the respective experimental ones in most cases. This difference indicates that not all types of ion–ion interactions have been taken into account in our calculations. It is obvious that not only unlike-charged ion–ion interactions but also interactions between like-charged ions and interactions between three ions (cation$_i$–cation$_j$–anion and anion$_i$–anion$_j$–cation) in the form of mixing parameters $\Theta^V_{i,j}$ and $\psi^V_{i,j,k}$ should be taken into account for precise volumetric calculations by the Pitzer ion interaction approach. The use of the mixing parameters, we are sure, will narrow the gap between the experimental and calculated densities and apparent molal volumes for multiple component electrolyte solutions. As demonstrated earlier [Krumgalz et al. (1995)] for 298.15 K, such mixing parameters $\Theta^V_{i,j}$ and $\psi^V_{i,j,k}$ were very important for precise volumetric calculations applied for mixed electrolyte solution systems and natural waters. However, since precise density data at various temperatures for ternary solutions either with a common cation or with a common anion are very occasional, the calculation of mixing parameters $\Theta^V_{i,j}$ and $\psi^V_{i,j,k}$ was impossible at this state of our knowledge.

6. Acknowledgments

This research was supported by Grant No. 89-00136 from the U.S.–Israel Binational Science Foundation (BSF), by Grant No. 27/00-1 from Israel Academy of Science, and by the Ministry of Energy and Infrastructure, Jerusalem, Israel. The work at Berkeley was assisted by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering and Geosciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors thank the referees of our manuscript whose very valuable comments helped us to improve the presentation of our results.

7. References

Adams, L. H., J. Am. Chem. Soc. **54**, 2229 (1932).

Allred, G. C. and E. M. Woolley, J. Chem. Thermodyn. **13**, 147 (1981).

Atkinson, G., A. Kumar, and B. L. Atkinson, AIChE J. **32**, 1561 (1986).

Baabor, S. J. and E. J. Delgado, Bol. Soc. Chil. Quim. **36**, 217 (1991).

Berecz, E. and I. Bader, Acta Chim. **77**, 285 (1973).

Bjerrum, N., Kgl. Danske Videnskab, Selskab, Mats.-Fys. Medd. **7**, 9 (1926).

Chen, C.-T. A., J. H. Chen, and F. J. Millero, J. Chem. Eng. Data **25**, 307 (1980).

Chen, C.-T. A., R. T. Emmet, and F. J. Millero, J. Chem. Eng. Data **22**, 201 (1977).

Connaughton, L. M. and F. J. Millero, J. Sol. Chem. **16**, 491 (1987).

Connaughton, L. M., J. P. Hershey, and F. J. Millero, J. Sol. Chem. **15**, 989 (1986).

Connaughton, L. M., F. J. Millero, and K. S. Pitzer, J. Sol. Chem. **18**, 1007 (1989).

Dedick, E. A., J. P. Hershey, S. Sotolongo, D. J. Stade, and F. J. Millero, J. Sol. Chem. **19**, 353 (1990).

Desnoyers, J. E., M. Arel, G. Perron, and C. Jolicoeur, J. Phys. Chem. **73**, 3346 (1969).

Dessauges, G., N. Miljevic, and A. Van Hook, J. Phys. Chem. **84**, 2588 (1980).

Drucker, C., Arkiv Kemi Min. Geol. **22a**, 1 (1946).

Dunn, L. A., Trans. Faraday Soc. **62**, 2348 (1966)

Dunn, L. A., Trans. Faraday Soc. **64**, 1898 (1968).

Ellis, A. J., J. Chem. Soc. A, 1138 (1968).

Emara, M. M. and N. A. Farid, J. Indian Chem. Soc. **58**, 474 (1981).

Fabuss, B. M., A. Korosi, and A. K. M. Shamsul, J. Chem. Eng. Data **11**, 325 (1966).

Fernandez, D. P., A. R. H. Goodwin, E. W. Lemmon, J. M. H. Sengers Levelt, and R. C. Williams, J. Phys. Chem. Ref. Data **26**, 1125 (1997).

Firth, J. G. and H. J. V. Tyrrell, J. Chem. Soc. 2042 (1962).

Fortier, J.-L., P.-A. Leduc, and J. E. Desnoyers, J. Sol. Chem. **3**, 323 (1974).

Franks, F. and H. T. Smith, Trans. Faraday Soc. **63**, 2586 (1967).

Gardner, A. W. and E. Glueckauf, Proc. R. Soc. London, Ser. A **321**, 515 (1971).

Gates, Y. A. and R. H. Wood, J. Chem. Eng. Data **30**, 44 (1985).

Geffcken, W., Z. Phys. Chem. **A155**, 1 (1931).

Geffcken, W. and D. Price, Z. Phys. Chem. **B26**, 81 (1934).

Gibson, R. E., J. Phys. Chem. **38**, 319 (1934).

Goncalves, F. A. and J. Kestin, Ber. Bunsenges. Phys. Chem. **81**, 1156 (1977).

Goncalves, F. A. and J. Kestin, Int. J. Thermophys. **2**, 315 (1981).

Gronwall, T. H., V. K. LaMer, and K. Sandved, Phys. Z. **29**, 358 (1928).

Grzybkowski, W. and G. Atkinson, J. Chem. Eng. Data **31**, 309 (1986).

Guggenheim, E. A., Trans. Faraday Soc. **55**, 1714 (1959).

Guggenheim, E. A., Trans. Faraday Soc. **56**, 1152 (1960).

Harr, L., J. S. Gallagher, and G. S. Kell, NBS/NRC Steam Tables. Thermodynamic and Transport properties and Computer programs for vapor and liquid states in SI Units. Hemisphere Publishing Corporation, pp. 5, 9, 301 (1984).

Halasey, M. E., J. Phys. Chem. **45**, 1252 (1941).

Hershey, J. P., S. Sotolongo, and F. J. Millero, J. Sol. Chem. **12**, 233 (1983).

Herz, W., Z. Anorg. Chem. **89**, 393 (1914).

Hölemann, P. and H. Kohner, Z. Phys. Chem. **B13**, 338 (1931).

I.C.T., *International Critical Tables* (McGraw–Hill, New York, 1928).

Isono, T., Rikagaku Kenkyusho Hokoku **56**, 103 (1980).

Isono, T., J. Chem. Eng. Data **29**, 45 (1984).

Isono, T., Rikagaku Kenkyusho Hokoku **61**, 53 (1985).

Jakli, G. Y., S. Cooper, R. S. Hutchings, and W. A. Van Hook, Acta Chim. Hung. **114**, 365 (1983).

Jones, G. and C. F. Bickford, J. Am. Chem. Soc. **56**, 602 (1934).

Jones, G. and S. M. Christian, J. Am. Chem. Soc. **59**, 484 (1937).

Jones, G. and J. H. Colvin, J. Am. Chem. Soc. **62**, 338 (1940).

Jones, G. and W. A. Ray, J. Am. Chem. Soc. **59**, 187 (1937).

Jones, G. and W. A. Ray, J. Am. Chem. Soc. **63**, 288 (1941).

Jones, G. and S. K. Talley, J. Am. Chem. Soc. **55**, 624 (1933a).

Jones, G. and S. K. Talley, J. Am. Chem. Soc. **55**, 4124 (1933b).

Kaminsky, M., Z. Phys. Chem. N. F. **12**, 206 (1957).

Karapet'yants, M. K., V. A. Vasilev, B. V. Mikhailin, and V. N. Strakhov, Russ. J. Phys. Chem. **53**, 111 (1979).

Kawaizumi, F., F. Nakao and H. Nomura, J. Chem. Eng. Data **33**, 204 (1988).

Kell, G. S., J. Chem. Eng. Data **20**, 97 (1975).

Kohner, H., Z. Phys. Chem. **B1**, 427 (1928).

Korosi, A. and B. M. Fabuss, Chem. Eng. Data **13**, 548 (1968).

Kruis, A., Z. Phys. Chem. **B34**, 1 (1936).

Krumgalz, B. S., J.C.S. Faraday I **76**, 1887 (1980).

Krumgalz, B. S., J.C.S. Faraday I **78**, 1327 (1982).

Krumgalz, B. S. and F. J. Millero, Mar. Chem. **11**, 477 (1982).

Krumgalz, B. S., R. Pogorelsky, Ya. A. Iosilevskii, A. Weiser, and K. S. Pitzer, J. Sol. Chem. **23**, 849 (1994).

Krumgalz, B. S., R. Pogorelsky, and K. S. Pitzer, J. Sol. Chem. **24**, 1025 (1995).

Krumgalz, B. S., R. Pogorelsky, and K. S. Pitzer, J. Phys. Chem. Ref. Data **25**, 663 (1996).

Kumar, A., Can. J. Chem. **63**, 3200 (1985).

Kumar, A., J. Chem. Eng. Data **31**, 19 (1986a).

Kumar, A., J. Chem. Eng. Data **31**, 21 (1986b).

Kumar, A., J. Solut. Chem. **15**, 409 (1986c).

Kumar, A., J. Chem. Eng. Data **32**, 106 (1987a).

Kumar, A., Chem. Eng. Data **32**, 109 (1987b).

Kumar, A., Monatshefte Fur Chemie **119**, 1201 (1988a).

Kumar, A., J. Chem. Eng. Data **33**, 198 (1988b).

Kumar, A., Chem. Eng. Data **34**, 87 (1989).

Kumar, A. and G. Atkinson, J. Phys. Chem. **87**, 5504 (1983).

Kumar, A., G. Atkinson, and R. D. Howell, J. Sol. Chem. **11**, 857 (1982).

Lanman, E. H. and B. Y. Mair, J. Am. Chem. Soc. **56**, 390 (1934).

Lengyel, S., J. Tamas, J. Giber, and J. Holderith, Acta Chim. Hung. **40**, 125 (1964).

Lo Surdo, A., E. M. Alzola, and F. J. Millero, J. Chem. Thermodyn **14**, 649 (1982).

Lyons, P. A. and J. F. Riley, J. Am. Chem. Soc. **76**, 5216 (1954).

MacInnes, D. A. and M. O. Dayhoff, J. Am. Chem. Soc. **74**, 1017 (1952).

Masson, D. O., Philos. Mag. Ser., **8**, 218 (1929).

Miller, D. G., J. A. Rard, L. B. Eppstein, and J. G. Albright, J. Phys. Chem. **88**, 5739 (1984).

Millero, F. J., Rev. Sci. Instrum. **38**, 1441 (1967).

Millero, F. J., J. Phys. Chem. **74**, 356 (1970).

Millero, F. J., "The Partial Molal Volumes of Electrolytes In Aqueous Solutions," in *Structure and Transport Process In Water and Aqueous Solutions*, edited by R. A. Horne (Wiley, New York, 1972a), Chap. 13, p. 519.

Millero, F. J., "Compilation of The Partial Molal Volumes of Electrolytes At Infinite Dilution, $\bar{V}^0$, and The Apparent Molal Volume Concentration Dependence Constants, S_v^* and B_v, At Various Temperatures," in *Structure and Transport Process In Water and Aqueous Solutions*, edited by R. A. Horne (Wiley, New York, 1972b), Addendum to Chap. 13, p. 565.

Millero, F. J. and W. Drost-Hansen, J. Chem. Eng. Data **13**, 330 (1968).

Millero, F. J. and J. H. Knox, J. Chem. Eng. Data **18**, 407 (1973).

Millero, F. J., E. V. Hoff, and L. Kahn, J. Sol. Chem. **1**, 309 (1972).

Millero, F. J., G. K. Ward, and P. V. Chetirkin, J. Acoust. Soc. Am. **61**, 1492 (1977).

Millero, F. J., L. M. Connaughton, F. Vinokurova, and P. Chetirkin, J. Sol. Chem. **14**, 837 (1985).

Monnin, C., J. Sol. Chem. **16**, 1035 (1987).

Monnin, C., Geochim. Cosmochim. Acta **53**, 1177 (1989).

Monnin, C., Geochim. Cosmochim. Acta **54**, 3265 (1990).

Nowicka, B., A. Kasperska, J. Barczynska, A. Bald, and S. Taniewska-Osinska, J. Chem. Soc. Faraday Trans. I **84**, 3877 (1988).

Oakes, C. S., J. M. Simonson, and R. J. Bodnar, J. Chem. Eng. Data. **35**, 304 (1990).

Olofsson, I. V., J. Chem. Thermodyn. **11**, 1005 (1979).

Out, D. J. P. and J. M. Los, J. Sol. Chem. **9**, 19 (1980).

Owen, B. B. and S. R. Brinkley, Ann. (N.Y.) Acad. Sci. **51**, 753 (1949).

Pabalan, R. T. and K. S. Pitzer, Geochim. Cosmochim. Acta **51**, 829 (1987).

Palaty, Z., Chem. Biochem. Eng. Q. **5**, 145 (1991).

Pearce, J. N. and K. C. Eckstrom, J. Am. Chem. Soc. **59**, 2689 (1937).

Perron, G., J. E. Desnoyers, and F. J. Millero, Can. J. Chem. **52**, 3738 (1974).

Perron, G., J.-L. Fortier, and J. E. Desnoyers, J. Chem. Thermodyn. **7**, 1177 (1975).

Perron, G., A. Roux, and J. E. Desnoyers, Can. J. Chem. **59**, 3049 (1981).

Pesce, G., Z. Phys. Chem. **A160**, 295 (1932).

Phang, S. and R. H. Stokes, J. Sol. Chem. **9**, 497 (1980).

Picker. P.. E. Tremblay. and C. Jolicoeur. J. Sol. Chem. **3**, 377 (1974).

Pitzer, K. S., J. Chem. Soc., Faraday Trans. II **68**, 101 (1972).

Pitzer, K. S., J. Phys. Chem. **77**, 268 (1973).

Pitzer, K. S., "Theory: Ion Interaction Approach," in *Activity Coefficients In Electrolyte Solutions*, edited by R. M. Pytkowicz (CRC, Boca Raton, FL, 1979), Vol. 1, p. 157.

Pitzer, K. S., "Ion Interaction Approach: Theory and Data Correlation," in *Activity Coefficients In Electrolyte Solutions*, 2nd ed., edited by K. S. Pitzer (CRC, Boca Raton, FL, 1991), Chap. 3, p. 75.

Pitzer, K. S. and G. Mayorga, J. Sol. Chem. **3**, 539 (1974).

Rasaiah, J. C., J. Chem. Phys. **56**, 3071 (1972).

Redlich, O., J. Phys. Chem. **67**, 496 (1963).

Redlich, O. and D. M. Meyer, Chem. Rev. **64**, 221 (1964).

Rogers, P. S. Z. and K. S. Pitzer, J. Phys. Chem. Ref. Data **11**, 15 (1982).

Romankiw, L. A. and I. M. Chou, J. Chem. Eng. Data **28**, 300 (1983).

Rutskov, A. P., Zh. Prikl. Khim. **21**, 820 (1948).

Scott, A. F., and R. W. Wilson, J. Phys. Chem. **38**, 951 (1934).

Scott, A. F., V. M. Obenhaus, and R. W. Wilson, J. Phys. Chem. **38**, 931 (1934).

Shedlovsky, T. and A. S. Brown, J. Am. Chem. Soc. **56**, 1066 (1934).

Simard, M.-A. and J.-L. Fortier, Can. J. Chem. **59**, 3208 (1981).

Singh, N. P. and P. K. Tikoo, J. Electrochem. Soc. India **29**, 219 (1980).

Sohnel, O., P. Novotny, and Z. Solc, J. Chem. Eng. Data **29**, 379 (1984).

Spedding, F. H., M. J. Pikal, and B. O. Ayers, J. Phys. Chem. **70**, 2440 (1966).

Spitzer, J. J., P. P. Singh, K. G. McCurdy, and L. G. Hepler, J. Sol. Chem. **7**, 81 (1978).

Stakhanova, M. S. and V. A. Vasilev, Russ. J. Phys. Chem. **37**, 839 (1963).

Trimble, H. M., J. Am. Chem. Soc. **44**, 451 (1922).

Vasilev, Y. A., N. V. Fedyainov, and V. V. Kurenkov, Russ. J. Phys. Chem. **47**, 1570 (1973)

Vaslow, F., Oak Ridge National Laboratory, Report Ornl-Tm-1438, (1966), 9 pp.

Vaslow, F., J. Phys. Chem. **73**, 3745 (1969).

Wirth, H. E., J. Am. Chem. Soc. **59**, 2549 (1937).

Wirth, H. E., J. Am. Chem. Soc. **62**, 1128 (1940).